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EVALUATION OF THE INTRINSIC METAL BINDING CAPACITY OF KRAFT BLACK LIQUOR LIGNINS

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ABSTRACT

Current and future environmental performance regulations will necessitate the reduction in the amounts of fresh water employed in the manufacturing of kraft pulps. It is now well appreciated that these changes will lead to an increase in nonprocess elements (NPEs) in various process streams. Perhaps one of the simplest methods of removing NPEs from a kraft mill is by optimizing their association with kraft black liquor lignins. Unfortunately, to date little is known of the fundamental principles contributing to the association of black liquor lignins (BLLs) with NPEs such as Mn, Mg, Ca, Ba, and Fe. This paper examines the relative metal binding capacity of BLLs and the functional groups in lignin that potentially contribute to this effect. A series of conventional and extended modified continuous kraft dissolved lignins were isolated and characterized employing modern NMR techniques. The affinity of BLLs for calcium and barium in a weak sodium hydroxide solution was studied at room temperature. The results of the metal binding studies were then correlated to the functional groups present in lignin.

INTRODUCTION

The design and operation of a minimum impact mill has become an important goal for pulp and paper research. One of the main problems associated with closure of a chemical pulp mill is the concern over the buildup of NPEs in various process streams. NPEs can cause problems in chemical recovery, bleaching, and on the paper machine. Amongst the most troublesome NPEs introduced into the pulp mill are calcium, manganese, and barium. Calcium and barium are known to cause scaling problems and manganese causes decomposition of hydrogen peroxide in the bleach plant (1).

The introduction of most NPEs into the pulp mill occurs primarily from the wood. The first partitioning of NPEs happens during pulping whereby metals can associate either with the pulp or black liquor. An unknown aspect of this partitioning effect is the association of NPEs with dissolved lignin in the black liquor. To explore the fundamental chemical interactions of NPEs with BLLs, a series of conventional and extended modified continuous kraft cooks were performed on a common wood source. The black liquors from these cooks were collected and the lignin was isolated using literature procedures (2). The relative metal binding affinity of these lignin samples for calcium and barium in a dilute sodium hydroxide solution was

determined. The contents of various lignin functional groups were determined by NMR spectroscopy and these results were then correlated with the results of the metal binding experiments.

EXPERIMENTAL

Materials

All chemicals were commercially purchased and used as received except for p-dioxane, which was purified by distillation over sodium borohydride. All pulps were prepared from a single *Pinus taeda* tree grown in the southeastern part of the USA. The tree was debarked, chipped, and screened. On average, chip thickness varied between 2 - 8 mm. Regenerated cellulose dialysis bags (Spectra/Por®) with a molecular weight cut-off of 1,000 were employed for all metal binding studies.

Kraft Pulping

Kraft pulping experiments were performed on a laboratory scale using well-established procedures that simulated conventional and extended modified continuous (i.e., Lo-Solids®) cooking (3). Table 1 highlights some of the pulping parameters employed and physical pulp properties.

Table 1. Pulping parameters and physical pulp properties.

Cook Type	Kappa #	Viscosity (mPas)	Max Cooking Temp. (°C)	H-factor	Total EA Consumed (% on wood)
Conventional	33.0	32.6	168.0	1201	14.8
Conventional	21.3	22.6	170.0	1999	15.4
Conventional	13.9	13.1	171.0	4000	16.9
Extended Modified	29.3	43.4	160.3	2003	14.1
Extended Modified	26.1	36.1	162.6	2442	15.2
Extended Modified	21.7	37.3	163.0	2504	17.7
Extended Modified	19.1	25.5	166.3	3362	15.0
Extended Modified	17.1	21.1	169.0	4126	15.9
Extended Modified	16.0	19.2	170.0	4489	16.6
Extended Modified	11.0	12.1	170.0	4474	17.8

Black Liquor Samples

The black liquor samples examined in this study were all end-of-cook samples. Hence, the black liquors from the conventional kraft cooks contain a composite mixture of lignin from throughout the cook. For the extended modified continuous kraft cooks, the end-of-cook black liquors are not a composite of all the lignin dissolved during the cook since the counter-current stage extracts black liquor.

Isolation of Lignin from Black Liquor

The procedure used for the isolation of lignin from black liquor was based upon literature methods (2). In brief, black liquor (50 mL, ~51 g) was diluted tenfold with distilled water and then treated with diethylenetriamine pentacetic acid (DTPA, 0.3-0.4 g). This solution was stirred for one hour and then acidified to pH 2 with an aqueous 1.00 N HCl solution. The resulting suspension was frozen, thawed, centrifuged, and the supernatant decanted. The isolated lignin was then redissolved in 0.01 N NaOH and the DTPA chelation process was repeated. After acidification, the precipitated lignin was washed thoroughly with distilled water and then dissolved with a 9:1 dioxane:water solution. The aqueous dioxane solution was filtered, concentrated under reduced pressure, and the resulting precipitate was collected and freeze dried. Finally, the lignin samples were soxhlet extracted with pentane for 8 h and then dried under high vacuum. ICP analysis of these lignins indicated that the metals Mn, Fe, Cu, Ba, Na, Mg, K, and Ca were nondetectable in the final purified form.

Lignin Ca^{2+}/Ba^{2+} Binding Capacity Determination

Purified lignin was dissolved in a sodium hydroxide solution (0.01 N) at a concentration of approximately 2 g/L. The lignin solution was then added to a 1,000 molecular weight dialysis bag and this was immersed in an aqueous 0.01 N sodium hydroxide solution. The outer solution was replaced several times with fresh 0.01 N NaOH solution so as to leach out all the low molecular weight lignin from the solution contained by the dialysis bag. The loss of low molecular weight lignin was monitored by TOC analysis. Typically, 10-20% of the lignin contained in the dialysis bag was lost during this leaching process, based on TOC analysis.

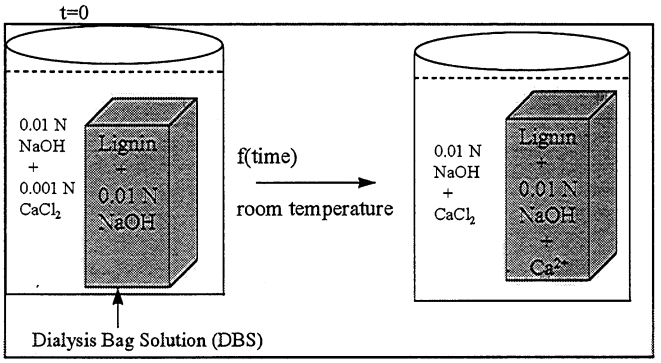
After no further lignin could be leached from the dialysis bag a sample of the lignin solution (25 mL, ~60-75 mg) was placed in a new solution containing 0.001 N $CaCl_2$ or $BaCl_2$ and 0.01 N NaOH (1000 mL). The migration of calcium into the dialysis bag solution was monitored by ICP. Typically, under our conditions the system reached equilibrium within 12 h.

^{31}P NMR Analysis

^{31}P NMR spectra were acquired on lignin samples that were derivatized with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane. This reagent phosphitylates hydroxyl groups, allowing indirect determination of hydroxyl-containing functional groups in lignin by quantitative ^{31}P NMR.

Each ^{31}P NMR acquisition was performed with a 25 sec delay between 90° pulses. An inverse gated decoupling pulse sequence was used to obtain quantitative spectra. A minimum of 100

Figure 1. Schematic of experimental procedure.



Employing this procedure, we were able to measure the relative lignin binding affinity for NPEs for a series of conventional and extended modified continuous kraft black liquor lignins. These measurements provide some of the first experimental data that demonstrates differences in black liquor lignin binding affinities for NPEs that can be related to the extent of delignification and pulping process employed. Furthermore, the mechanisms contributing to these differences were explored by determining the functional groups present in the lignin samples.

Calcium Binding

Lignin was isolated from kraft black liquors by acid precipitation following well established literature methods (2). The NPEs present in the BLLs were removed by adding DTPA to the black liquor solution prior to acid precipitation. The resulting lignin samples were then employed for a series of NPE binding studies.

Preliminary binding studies indicated that the kraft BLLs contained a small fraction of low molecular weight material that could readily diffuse through a dialysis bag having a 1,000 molecular weight cut off. The NPE binding studies were therefore performed only after all leachable lignin was removed from the dialysis bag solution (DBS). Based on TOC measurements, 10-20% of the lignin in the DBS could be removed after 36 hours exposure to a 0.01 N NaOH solution.

After the low molecular weight material was removed from the DBS the lignin solution was exposed to a fresh aqueous solution containing NaOH (0.010 N) and $CaCl_2$ (0.001 N). The incorporation of Ca^{2+} in the DBS was monitored by taking aliquots and determining Ca^{2+} concentration by ICP. All of the lignin samples studied in this report were found to exhibit selective affinity for calcium under the experimental conditions employed.

The calcium bound to lignin in the DBS was determined by subtracting the total calcium concentration inside the dialysis bag from the concentration in the outside solution. This calculation is based on the assumption that the free calcium inside the DBS is the same as the calcium concentration outside of the bag. This assumption was made on the basis of control experiments with no lignin in the dialysis bag. The control experiments show that when equilibrium is reached, the concentration inside and outside of the bag is the same. The relative calcium association with lignin was then determined by dividing the bound calcium concentration

by the lignin concentration to yield milligrams of calcium per gram of lignin. Figures 2 and 3 show the kappa number of the pulp versus the calcium binding capacity for each of the BLL sample. For the conventional kraft lignins, as pulp delignification was increased, an increase in the BLL binding capacity for calcium is observed (Figure 2). This trend is not observed for the BLLs isolated from the extended modified kraft pulps, as shown in Figure 3. The calcium binding capacity for extended modified BLL appears not to change substantially as pulp delignification proceeds.

Barium Binding

The relative barium binding capacity of the BLLs was determined in the same manner as the relative calcium binding capacity and these results are summarized in Figures 4 and 5. For the BLLs from the conventional kraft cooks, barium binding capacity (Figure 4) increases as the final kappa number of the pulp decreases. The barium binding capacity for the extended modified continuous kraft lignins (Figure 5) exhibited little variation. Interestingly, BLLs from both the conventional and extended modified continuous kraft cooks exhibited higher affinity for barium ions than calcium under the conditions studied.

Investigations into BLL Binding Mechanisms for Ca/Ba

The fundamental mechanisms contributing to the binding association of calcium and barium to BLLs was explored by measuring lignin functional groups. Employing modern NMR techniques (4, 5, 6, 7) the carboxylic acid, aliphatic hydroxy groups, condensed and noncondensed phenoxy content of each BLL was determined. For the BLL samples isolated from the conventional kraft cooks a correlation was noted between the increase in metal binding affinity and an increase in the total concentration of acid groups and condensed phenolics present in the lignin samples (Table 3).

Table 3. Content of carboxylic acid groups and condensed phenoxy groups in conventional kraft BLL binding and their measured affinities for Ca^{2+} and Ba^{2+}.

Pulp kappa number for conventional BLL sample	mmol of carboxylic acids /g of lignin	mmol of condensed phenols/g of lignin	Bound Ca/g of lignin	Bound Ba/g of lignin
33.0	0.39	1.15	31.0	102
21.3	0.41	1.27	42.0	129
13.9	0.43	1.30	65.9	137

Unfortunately, no such relationship was observed for the BLLs isolated from the extended modified continuous kraft cooks. Several factors may be contributing to this difference including the fact that the conventional end-of-cook BLLs represent a composite sample of lignin released throughout the cook. Whereas, the end-of-cook extended modified continuous BLLs are not a composite of all the lignin dissolved during the cook since the counter-current stage extracts black liquor during the cook. Furthermore, it is anticipated that the conventional and extended modified continuous BLL samples have different molecular weight distributions and this could also influence the NPE binding affinities.

scans was acquired for each sample. The acquisitions were performed at room temperature, using a 61.9 ppm sweep width and a 4 Hz line broadening (TD = 32,768). Calibration of the chemical shifts and integration of the functional groups were accomplished as described in the literature (4, 5, 6, 7).

Variability

To determine variability associated with the NMR spectroscopy, one lignin sample was repeated a number of times. The results of statistical analyses are shown in Table 2.

Table 2. NMR variability data.

	Functional Groups (mmol/g isolated lignin)			
	Aliphatic OH	Condensed Phenolics	Non-Condensed Phenolics	Carboxylic Acids
Average	1.220	1.209	1.410	0.412
Std Dev	0.068	0.048	0.082	0.012
LSD*	0.275	0.194	0.328	0.048
*least significant difference t-value for 95 % confidence with 5 degrees of freedom is 2.01 LSD = 2 x (standard deviation) x (t-value)				

Randomly selected metal binding experiments were repeated to find information on variability. No experiment varied more than 15% from the value originally obtained.

RESULTS AND DISCUSSION

Recent studies by Ragauskas et al. have examined the differences in bleachability for a series of conventional and extended modified continuous kraft pulps (8). All these pulps were prepared from a common wood source and cooked with modern laboratory pulping facilities. These experiments provided not only a series of well-defined pulps but also a complete series of kraft black liquors. The availability of a series of well-defined and structurally characterized black liquor lignin samples provided the opportunity to examine the affinity of BLLs towards NPEs. In this preliminary report, we describe a method that provides a means of determining the relative binding affinity of black liquor lignin toward NPEs in a weak sodium hydroxide solution at room temperature. In brief, this was accomplished by dissolving lignin in an alkaline solution, placing this material in a dialysis bag and then immersing the dialysis bag in an alkaline solution containing an additional NPE, such as calcium or barium. The enhanced concentration of the NPE in the dialysis bag, at equilibrium, then becomes a relative measurement of the affinity for this metal under the conditions used (Figure 1).

SUMMARY AND RECOMMENDATIONS

In conclusion, a relatively facile method has been developed that allows for rapid screening of the NPE binding capacity of lignin. Our preliminary results suggest that BLL samples have different affinities for calcium and barium. Furthermore, the metal binding affinity for conventional BLL samples was influenced by the extent of delignification; whereas, the end-of-cook BLL samples from the extended modified pulps were less sensitive to the final kappa number of the pulp. Clearly, further studies need to be performed to fully identify the factors that contribute to NPE binding by BLLs and how these parameters may be operating under pulping conditions.

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APPENDIX

Figure 2. Calcium binding affinity versus kappa number of the pulp for conventional cooks.

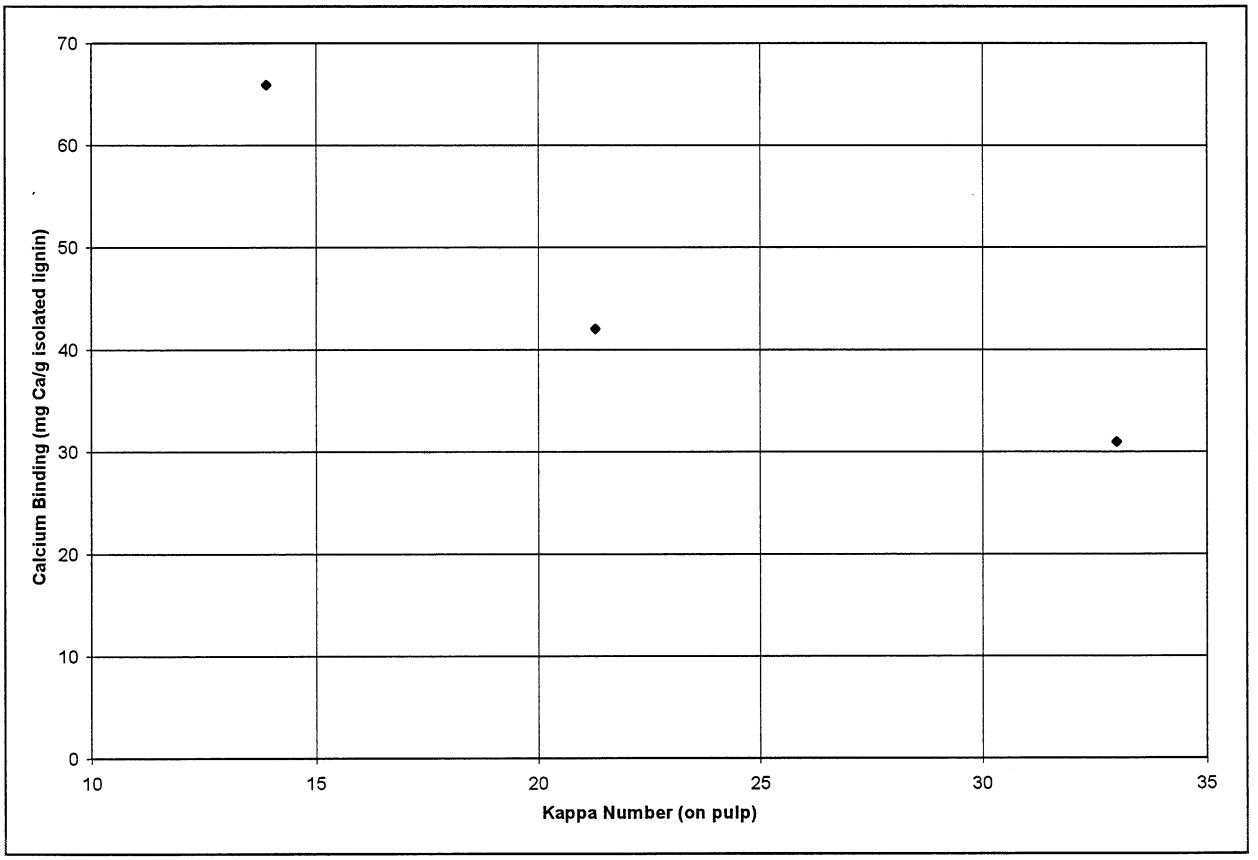

Figure 3. Calcium binding affinity versus kappa number of the pulp for extended modified cooks.

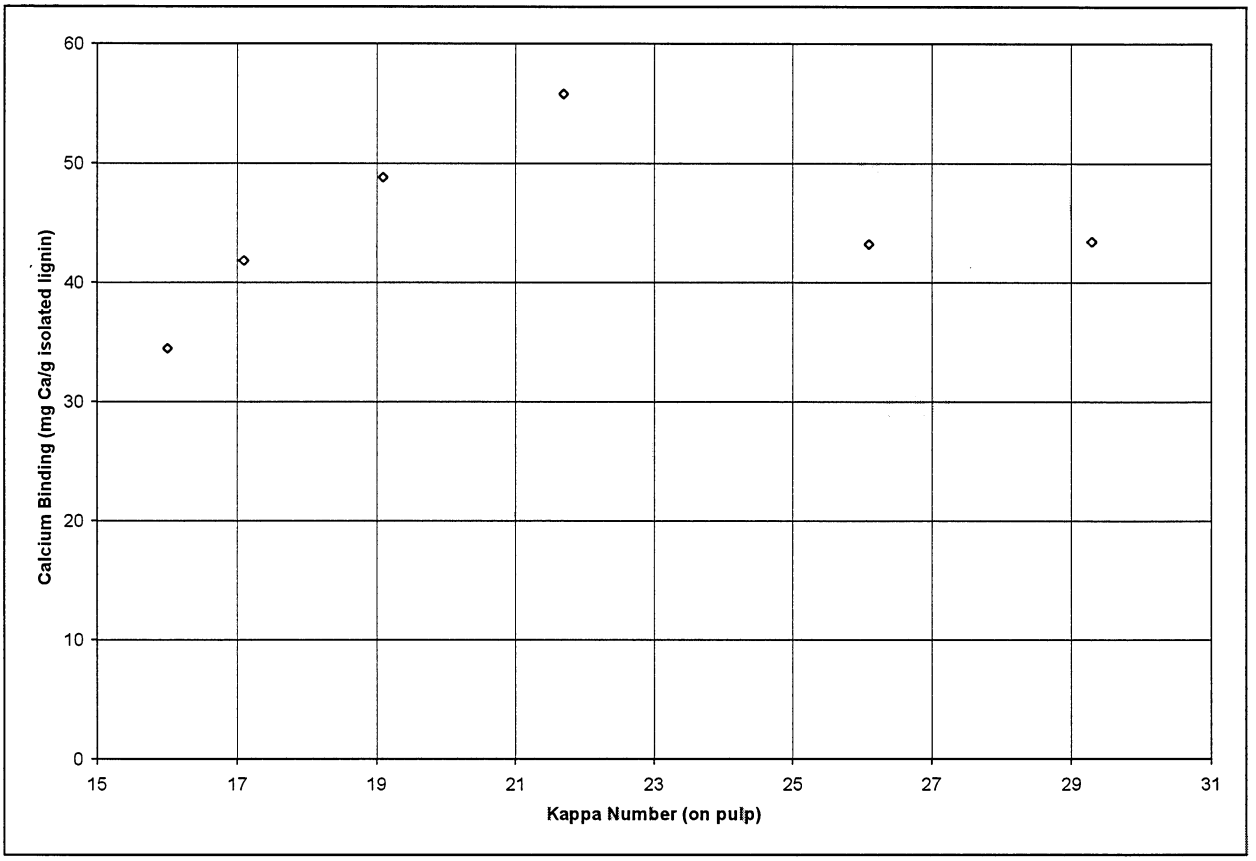

Figure 4. Barium binding affinity versus kappa number of the pulp for conventional cooks.

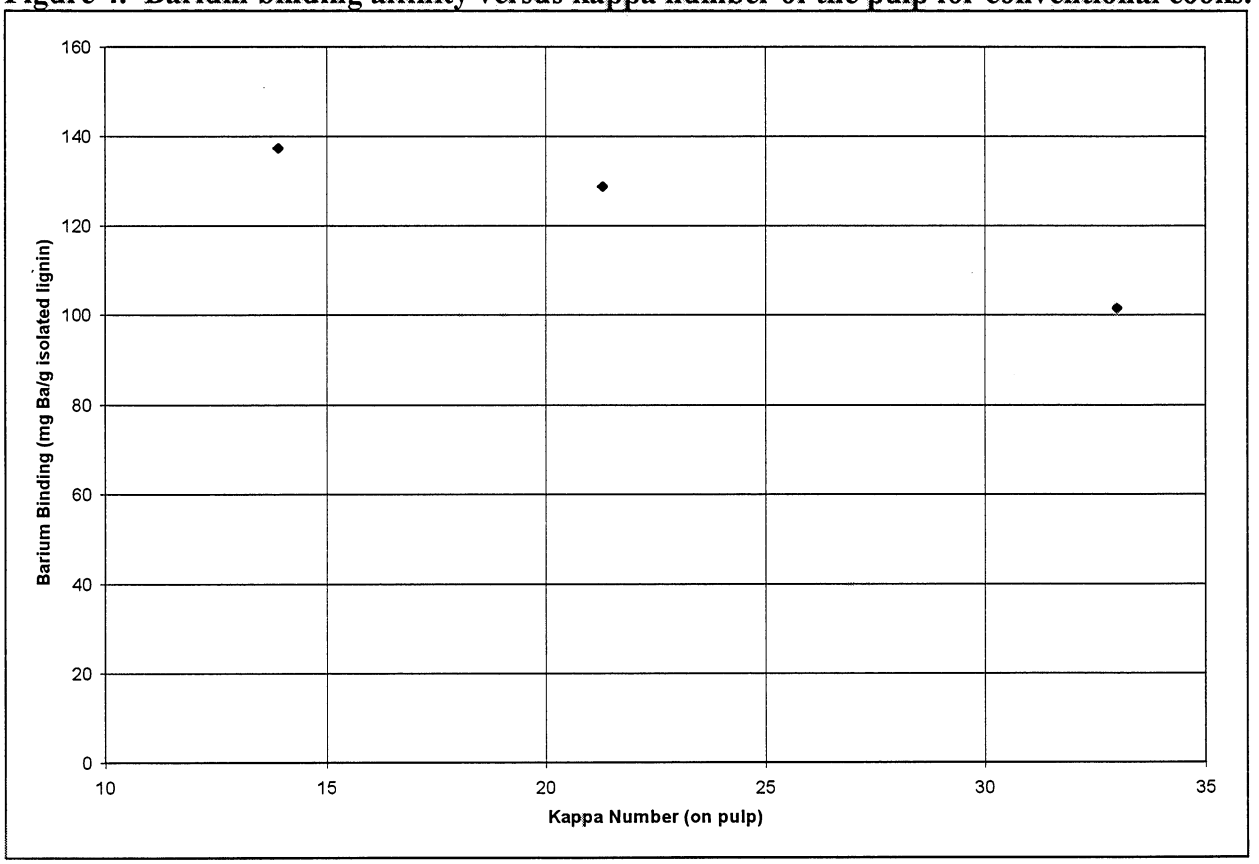

Figure 5. Barium binding affinity versus kappa number of the pulp for extended modified cooks.